

SUPRAMOLECULAR POLYMERS

Molecular machines muscle up

A supramolecular polymer made of thousands of bistable [c2]daisy chains amplifies individual nanometric displacements up to the micrometre-length scale, in a concerted process reminiscent of muscular cells.

Carson J. Bruns and J. Fraser Stoddart

One of the grand challenges at the forefront of bottom-up nanotechnology is to integrate artificial molecular machines (AMMs) — molecules that express controllable, stimuli-responsive mechanical motion^{1,2} — into larger systems in such a manner that individual nanoscopic displacements couple to perform a useful task³. However, it remains extremely challenging to amplify the motion of AMMs to the macroscopic regime, similar to what muscle cells do by way of synchronized action in hierarchically organized myosin and actin filaments. Taking an important step towards this goal, Nicolas Giuseppone, Eric Buhler and co-workers describe in *Angewandte*

Chemie a metallosupramolecular polymer that scales the contraction and extension of its repeating units over several orders of magnitude — from nanometres to micrometres — in a muscle-like fashion⁴.

The molecular platform hinges on the widely used supramolecular recognition motif^{5,6} between a secondary dialkylammonium ion, NH_2^+ , (blue; Fig. 1) and a [24]crown-8 (red rings; Fig. 1). This motif has been used extensively in the template-directed synthesis of rotaxanes — molecules in which a ring encircles a rod component with end groups that are sufficiently bulky to prevent the ring from slipping off. Because the affinity of the NH_2^+ unit for the crown ether is mediated by its positive charge and hydrogen-

bonding interactions, the recognition can be deactivated by transforming the ammonium ion into the corresponding neutral amine (light blue; Fig. 1) at higher pH. This reversible, pH-dependent complexation has been exploited in the production of bistable rotaxanes, AMMs in which a ring translates between two 'stations' along a rod in response to an appropriate stimulus⁷. Giuseppone and Buhler, who are based at the University of Strasbourg and University of Paris Diderot, France, respectively, use pH-switchable bistable [c2]daisy chains, a class of rotaxanes in which two self-complementary monomers comprising an end group and rod attached covalently to a ring are cross-threaded into a cyclic

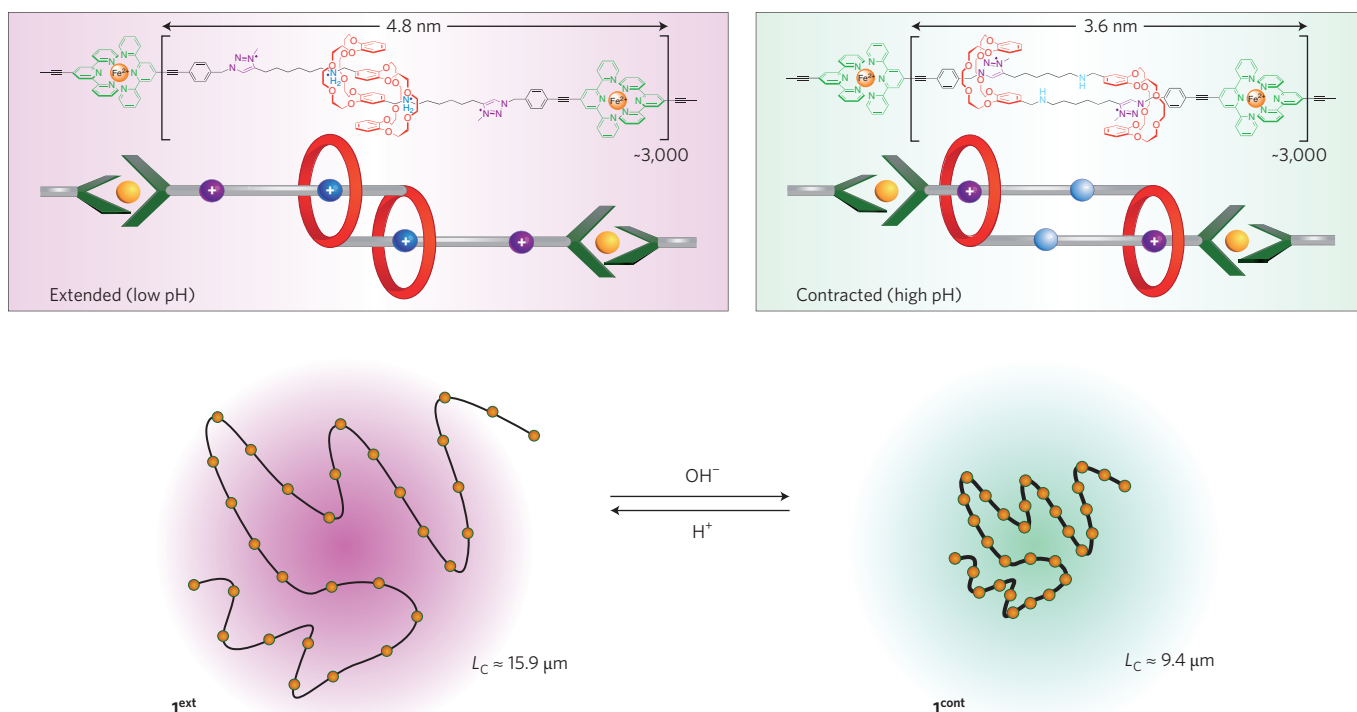


Figure 1 | Amplification of muscle-like mechanical actuation within a metallosupramolecular [c2]daisy chain polymer **1**. With the daisy chain units in their extended geometry at low pH (left), the total length of the polymer **1**^{ext} is estimated to be ~15.9 μm by neutron scattering experiments. At higher pH (right), a ~1.2 nm contraction of the repeating units shortens the polymer length of **1**^{cont} to ~9.4 μm, corresponding to an amplification of nanoscopic motion by over three orders of magnitude as a result of ~3,000 artificial molecular machines operating coherently in the same polymer chain. Dialkylammonium ion (NH_2^+), blue; [24]crown-8, red; neutral amine, light blue; triazolium units, purple; terpyridine, green.

dimer. Jean-Pierre Sauvage pioneered the study of bistable [c2]daisy chains more than a decade ago^{8–10}, noting that switching the rings between two positions along the respective rods corresponds to a significant change in the overall length of the molecule. Although Sauvage's transformation was triggered by transition-metal-ion exchange, pH-switchable daisy chains based on NH_2^+ and [24]crown-8 have subsequently emerged^{11–13}.

Bistable daisy chains have also been incorporated covalently into polymers, but the low degree of polymerization that can be achieved (≤ 22 monomer units) has precluded any significant scaling up of individual mechanical motions^{13,14}. The French groups achieved a high degree of polymerization ($\sim 3,000$ units) by choosing a metallocupramolecular approach to polymerizing their daisy chains. The procedure involves installing terpyridine (green; Fig. 1) end-groups, which form stable octahedral 2:1 complexes with certain transition metal ions. The pairing of terpyridine end-groups around Fe^{2+} ions in solution drives the linear polymerization of the daisy chains to yield the metallocupramolecular polymer **1**. (Fe^{2+} works particularly well compared with for example, Zn^{2+} , because its higher affinity for terpyridine promotes the formation of longer, more robust polymers that are more stable to pH changes.)

The functional properties of the polymer were investigated by neutron scattering — a powerful technique used to extract reliable size and shape parameters

from solvated objects in solution in the nanometre- to micrometre-size range. At low pH, the NH_2^+ recognition sites in **1** are preferentially encircled and the daisy chains adopt the 'extended' geometry **1^{ext}**. At higher pH, these recognition sites are deactivated and the rings move to encircle the permanently charged triazolium units (purple; Fig. 1), adopting the 'contracted' geometry **1^{cont}**. The extended and contracted monomer units measure 4.8 and 3.6 nm in length, respectively. Neutron scattering reveals that variations in pH are accompanied by significant structural changes within the polymer. Although both states express identical degrees of polymerization, the contour length, L_C (that is, the total length of the polymer at full extension) and the linear mass density, M_L (that is, the average mass of the polymer per unit of length) differ dramatically. **1^{ext}** is long and skinny ($L_C \sim 15.9 \mu\text{m}$, $M_L \sim 500 \text{ g mol}^{-1} \text{ nm}^{-1}$), whereas **1^{cont}** is relatively short and fat ($L_C \sim 9.4 \mu\text{m}$ and $M_L \sim 750 \text{ g mol}^{-1} \text{ nm}^{-1}$). The contraction in total length ($\Delta L_C \sim -6.5 \mu\text{m}$) is inversely proportional to its change in linear mass density ($\Delta M_L \sim +250 \text{ g mol}^{-1} \text{ nm}^{-1}$) and agrees well with a mechanistic model involving concerted actuation of the individual daisy chain units.

These tiny daisy chains, which individually actuate on a length scale of about 1 nm, can produce a global change in length exceeding $6 \mu\text{m}$ when integrated in large numbers into a microscopic polymer. It is this kind of major scale-up that is

required to coerce AMMs into doing work in the macroscopic world. The challenge that lies ahead for these switchable mechanically interlocked polymer chains is to align and bundle them into stimuli-responsive fibres that can comprise artificial muscle materials^{3,4}. \square

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SUPERCONDUCTIVITY

The imaginary is real

Experiments on nano-islands of a high-temperature superconductor reveal the presence of a small imaginary component of the superconducting order parameter.

Guy Deutscher

Superconductors are characterized by the absence of electrical resistivity below a critical temperature T_C . The absence of resistivity is due to the formation of pairs of electrons of opposite momenta and spins (known as Cooper pairs). Although Cooper pairs are common to all superconductors, the pairing mechanism can vary. In superconducting metals and alloys, which have a T_C lower than 30 K, the pairing is due to the electron–phonon interaction. In the

high-temperature superconductors of the cuprate class however, the mechanism is still under debate.

The superconducting state is characterized by a so-called order parameter, which is zero above T_C , and has an amplitude and a phase below T_C . More precisely, the amplitude coincides with the energy necessary to break a Cooper pair, also known as the superconducting gap Δ . Knowledge of the symmetry of the order parameter is essential for understanding

the superconducting mechanism. The electron–phonon interaction usually leads to an *s*-type symmetry, with uniform phase and amplitude. On the contrary, some mechanisms that have been proposed to explain high-temperature superconductivity are purely electronic and lead to a strongly anisotropic order parameter of the $d_{x^2-y^2}$ type, with nodes and a phase change of π at 45° from the principal axis of the CuO_2 plane (Fig. 1). Now writing in *Nature*